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Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Comparison of a Nitric Acid In-Bottle Digestion Procedure to Other Whole-Water Digestion Procedures

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By John R. Garbarino and Gerald L. Hoffman

U.S. GEOLOGICAL SURVEY

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CONVERSION FACTORS AND ABBREVIATED WATER-QUALITY UNITS

Multiply	By	To obtain
gram (g)	3.53×10^{-2}	ounce, avoirdupois
liter (L)	2.64×10^{-1}	gallon
microgram (µg)	3.53×10^{-8}	ounce, avoirdupois
milligram (mg)	3.53×10^{-5}	ounce, avoirdupois
milliliter (mL)	2.64×10^{-4}	gallon

Degree Celsius (°C) may be converted to degree Fahrenheit (°F) by using the following equation:

$$°F = 9/5\ (°C) + 32.$$

Abbreviated water-quality units used in this report are as follows:

mg/g	milligram per gram
µg/g	microgram per gram
µg/L	microgram per liter

Other abbreviations also used in this report:

ASTM	American Society for Testing and Materials
DCP–AES	direct current plasma–atomic emission spectrometry
F–AAS	flame–atomic absorption spectrophotometry
GF–AAS	graphite furnace–atomic absorption spectrophotometry
HCl	hydrochloric acid
HG–AAS	hydride generation–atomic absorption spectrophotometry
HNO_3	nitric acid
ICP–AES	inductively coupled plasma–atomic emission spectrometry, also known as inductively coupled plasma–optical emission spectrometry (ICP–OES)
ICP–MS	inductively coupled plasma–mass spectrometry
MPV(s)	most probable value(s)
N	normality (acid equivalents per liter)
NIST	National Institute of Standards and Technology
NWQL	National Water Quality Laboratory
SRM	Standard Reference Material
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
<	less than
±	plus or minus

Definitions:

MPV The most probable value (MPV) is equal to the median value for numerous interlaboratory analyses that use multiple analytical methods.

Whole-water recoverable. Pertains to the constituents in solution after a representative water-suspended-sediment sample is digested (usually using dilute acid solution). Complete dissolution of particulate matter often is not achieved by the digestion treatment, and thus the determination represents something less than the "total" amount (that is, less than 95 percent) of the constituent present in the dissolved and suspended phases of the sample. Equivalent digestion procedures would be required of all laboratories that perform such analyses to achieve comparability of analytical data, because different digestion procedures are likely to produce different analytical results.

Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Comparison of a Nitric Acid In-Bottle Digestion Procedure to Other Whole-Water Digestion Procedures

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ABSTRACT

A hydrochloric acid in-bottle digestion procedure is used to partially digest whole-water samples prior to determining recoverable elements by various analytical methods. The use of hydrochloric acid is problematic for some methods of analysis because of spectral interference. The in-bottle digestion procedure has been modified to eliminate such interference by using nitric acid instead of hydrochloric acid in the digestion. Implications of this modification are evaluated by comparing results for a series of synthetic whole-water samples. Results are also compared with those obtained by using U.S. Environmental Protection Agency (1994) (USEPA) Method 200.2 total-recoverable digestion procedure. Percentage yields that use the nitric acid in-bottle digestion procedure are within 10 percent of the hydrochloric acid in-bottle yields for 25 of the 26 elements determined in two of the three synthetic whole-water samples tested. Differences in percentage yields for the third synthetic whole-water sample were greater than 10 percent for 16 of the 26 elements determined. The USEPA method was the most rigorous for solubilizing elements from particulate matter in all three synthetic whole-water samples. Nevertheless, the variability in the percentage yield by using the USEPA digestion procedure was generally greater than the in-bottle digestion procedure, presumably because of the difficulty in controlling the digestion conditions accurately.

INTRODUCTION

The U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL) has been using the hydrochloric acid (HCl) in-bottle digestion procedure described by Hoffman and others (1996) since 1992. New analytical methods that expand the scope of elemental determinations, such as inductively coupled plasma–mass spectrometry (ICP–MS), have been developed that are adversely affected by the presence of HCl in the in-bottle digestate.

Implementation of newer methods for the determination of elements in whole-water samples, therefore, requires modification of the in-bottle procedure. The proposed modification involves using nitric acid (HNO_3) instead of HCl for the in-bottle digestion. The bias and variability of such a modification were determined by digesting three synthetic whole-water samples by the HCl and the HNO_3 in-bottle procedures. Replicate samples were also digested using U.S. Environmental Protection Agency (1994) (USEPA) Method 200.2 as an additional comparison. Elements currently (1999) being determined in HCl in-bottle

digestate and their corresponding USGS analytical methods are listed in table 1.

The objectives of this report are as follows:

- To describe the HNO_3 in-bottle digestion procedure.
- To establish the bias and variability of the HNO_3 in-bottle digestion procedure.
- To discuss the advantages and disadvantages of using the HNO_3 in-bottle digestion procedure.

The subject method was developed by the USGS for use at the NWQL. This method supplements other official USGS inorganic methods (Fishman and Friedman, 1989; Fishman, 1993).

ANALYTICAL METHOD

Metals, Extraction Procedure, Acid Digestion, Whole-Water Recoverable, I-3487-98

1. Application

This method was developed to digest whole-water samples by using an HNO_3 in-bottle procedure to determine the elements listed in table 1.

2. Summary of Method

Hoffman and others (1996) have previously described an HCl in-bottle digestion procedure. The HNO_3 in-bottle procedure requires minor modifications to the HCl in-bottle procedure as outlined in section 6. After the preparatory procedure, the digestate can be analyzed by using any of the methods listed in table 1. Details of these analytical methods can be obtained in Fishman (1993), Fishman and Friedman (1989), Garbarino and Struzeski (1998), and Jones and Garbarino (1999).

3. Interferences

There are no known interferences associated with procedures described in this report.

4. Apparatus and Materials

4.1 *Clean bench,* class-100.

4.2 *Filter paper,* Whatman No. 41 or equivalent.

4.3 *Disposable filter funnels,* Whatman No. 1920-1441 or equivalent.

4.4 *Drying oven,* mechanical convection heating, with controlled time and temperature accurate to ±1 percent.

4.5 *Analytical balance,* Mettler Model PM600 or equivalent capable of accurately weighing 0.01 g.

4.6 *Sample bottles,* made of polyethylene or polypropylene.

4.7 *Filter-funnel racks,* variable height adjustable, nonmetallic construction that tolerates dilute acid.

5. Reagents

5.1 *Nitric acid (HNO_3)*, concentrated (specific gravity 1.41), a grade verified to have elemental contaminant concentrations, after the prescribed dilution, that are less than the method detection limits for the method of analysis being used.

Table 1. Methodologies used to determine whole-water recoverable elements in the hydrochloric acid in-bottle digestate

[Method, analytical methods are listed in the order of decreasing method detection limit; DCP–AES, direct current plasma–atomic emission spectrometry; ICP–AES, inductively coupled plasma–atomic emission spectrometry; ICP–MS, inductively coupled plasma–mass spectrometry; HG–AAS, hydride generation–atomic absorption spectrophotometry; GF–AAS, graphite furnace–atomic absorption spectrophotometry; F–AAS, flame–atomic absorption spectrophotometry]

Element or constituent	Lab codes	Method	Element or constituent	Lab codes	Method
Aluminum	1283	DCP–AES	Lithium	277	F–AAS
	2351	ICP–AES		2361	ICP–AES
	2372	ICP–MS		2381	ICP–MS
Antimony	80	HG–AAS	Magnesium	261	F–AAS
	2373	ICP–MS		2362	ICP–AES
Arsenic	118	HG–AAS	Manganese	41	F–AAS
	2162	GF–AAS		2363	ICP–AES
Barium	234	F–AAS		2382	ICP–MS
	2352	ICP–AES	Molybdenum	2364	ICP–AES
	2374	ICP–MS		1999	GF–AAS
Beryllium	236	F–AAS		2383	ICP–MS
	2353	ICP–AES	Nickel	198	F–AAS
	2375	ICP–MS		2365	ICP–AES
Boron	1286	DCP–AES		1563	GF–AAS
	2354	ICP–AES		2384	ICP–MS
Cadmium	131	F–AAS	Potassium	321	F–AAS
	2355	ICP–AES	Selenium	286	HG–AAS
	1555	GF–AAS		2163	GF–AAS
	2376	ICP–MS		2385	ICP–MS
Calcium	244	F–AAS	Silica (SiO_2)	2366	ICP–AES
	2356	ICP–AES	Silver	2367	ICP–AES
Chromium	246	F–AAS		1553	GF–AAS
	1937	GF–AAS		2386	ICP–MS
	2377	ICP–MS	Sodium	320	F–AAS
Cobalt	149	F–AAS		2368	ICP–AES
	2391	ICP–AES	Strontium	290	F–AAS
	1557	GF–AAS		2369	ICP–AES
	2378	ICP–MS		2387	ICP–MS
Copper	156	F–AAS	Thallium	2388	ICP–MS
	2358	ICP–AES	Uranium	2389	ICP–MS
	1559	GF–AAS	Vanadium	2370	ICP–AES
	2379	ICP–MS	Zinc	296	F–AAS
Iron	189	F–AAS		2371	ICP–AES
	2359	ICP–AES		2390	ICP–MS
Lead	192	F–AAS			
	2360	ICP–AES			
	1561	GF–AAS			
	2380	ICP–MS			

5.2 *Water*, ASTM Type I reagent water (American Society for Testing and Materials, 1995).

5.3 *0.1N HNO_3 is* prepared by adding 6.4 mL of acceptable concentrated nitric acid to 500 mL of water and dilute to 1L with water.

6. Nitric Acid In-Bottle Digestion Procedure

Unfiltered, acidified (also known as raw acidified, RA) samples are digested by using the following procedure:

6.1 Weigh the sample bottle, cap, and contents to determine the gross weight.

6.2 Subtract the average weight of an identical size capped bottle to estimate the volume of the sample.

6.3 Add 1.6 mL of concentrated HNO_3 for every 50 mL (or about 3 percent by volume) of sample.

6.4 Recap the bottle and shake vigorously.

NOTE 1: Prepare a reagent blank and a synthetic whole-water sample with each set of samples digested (see sections 6.1–6.4).

6.5 Place the capped sample bottles in a 65°C oven and heat the samples for 8 hours. Heating time includes the time required for the samples to reach oven temperature.

6.6 *Preparation for filtering sample digestate*

6.6.1 Open the sealed disposable filter funnels inside the clean bench and place in the filter-funnel rack.

6.6.2 Rinse each funnel by rapidly filling with 250 mL of 0.1*N* HNO_3; repeat rinsing with another 250 mL of 0.1*N* HNO_3.

6.6.3 Similarly rinse each funnel three times with water. Allow the funnels to drain completely between each rinse.

6.7 *Sample digestate filtration*

6.7.1 Place a clean, empty, acid-rinsed and labeled bottle under each funnel.

6.7.2 Vigorously shake the sample bottle containing digestate after it has been removed from the oven. Let stand for 30 minutes, and filter aliquots of the digestate by using the filter funnel.

6.7.3 Discard unfiltered digestate. Rinse the original sample bottle twice with water and dispose of the rinse into a suitable container clearly labeled as acid waste.

6.7.4 Transfer filtrate (see section 6.7.2) into its original sample bottle and seal with a new, clear cap.

6.7.5 Use aliquots of this filtered solution to determine whole-water recoverable elemental concentrations by the appropriate analytical methods.

NOTE 2: Filtration of 100 percent of the digestate volume is not required if the sample bottles are shaken vigorously after removal from the oven. At least 75 percent of the sample must be filtered to ensure sufficient volume for multiple analyses.

NOTE 3: If a filter becomes plugged during filtration, replace it with a rinsed filter funnel and continue the filtration.

7. Calculations

No calculations are required.

8. Reporting Results

Whole-water recoverable concentrations are reported in micrograms per liter to the number of significant figures outlined in the analytical method being used for quantitation.

DISCUSSION OF RESULTS

Currently (1999), selected USGS methods are used to analyze the HCl in-bottle digestate. However, new methods that expand the scope of elemental determinations that are adversely affected by the presence of HCl in the in-bottle digestate have been developed. It is advantageous to have one in-bottle digestion procedure that is compatible with all the USGS methods used to determine the elements listed in table 1. Such a procedure is the HNO_3 in-bottle digestion. Its digestate is entirely compatible with all whole-water recoverable methods because HNO_3 does not cause spectral interferences. The extraction efficiency of HNO_3, however, is most likely different from that of HCl. All the digestion methods tested in this report are procedural and use different acids, acid concentrations, and methods of heating. For example, the USEPA procedure refluxes the digestate, whereas the in-bottle procedures do not.

The bias and variability associated with the HNO_3 in-bottle digestion procedure were determined by using results obtained for synthetic whole-water samples that were made from reference sediment. Synthetic whole-water samples are used as benchmarks in this study, as in the study by Hoffman and others (1996), because they are based on readily available certified reference materials and because the mixtures can be accurately reproduced.

The synthetic whole-water samples were prepared by weighing 200 to 600 mg of the National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 2704 Buffalo River Sediment, 1645 Riverine Sediment, or 1646 Estuarine Sediment into 200 to 500 mL of 0.1*N* HNO_3. Following preparation, the synthetic whole-water samples were shaken and allowed to stand at room temperature for about 3 days to simulate actual whole-water samples that are collected and acidified on-site. Four samples of each synthetic whole water were digested using the HCl in-bottle procedure (Hoffman and others, 1996), the HNO_3 in-bottle procedure, and the USEPA procedure. Aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, iron, lead, lithium, manganese, molybdenum, nickel, selenium, silver, strontium, thallium, uranium, vanadium, and zinc were determined in every synthetic whole-water digestate by ICP–MS. Calcium, iron, magnesium, silica (SiO_2), and sodium were determined by inductively coupled plasma–atomic emission spectrometry (ICP–AES). Potassium was determined by using flame–atomic absorption spectrophotometry (F–AAS). Aliquots of each HCl in-bottle and USEPA digestate were processed before ICP–MS analysis to remove chloride by using the procedure described in the Appendix of this report.

Elemental concentrations from ICP–AES, ICP–MS, and F–AAS for all synthetic whole-water digestates are listed in tables 2 through 4 with corresponding percentage yields listed in tables 5 through 7. Percentage yield was calculated from the concentration results by using equation 1.

$$\text{Percentage yield} = [(C_S \times V_S) / (C_R \times W_R)] \times 100 \quad (1)$$

where C_S is the elemental concentration (in micrograms per liter) in the digestate, V_S is the total volume (in liters) used to prepare the synthetic whole-water sample, C_R is the elemental concentration in the reference sediment (in micrograms per gram), and W_R is the weight of reference sediment (in grams) used to prepare the synthetic whole-water sample. Percentage yields listed in tables 5 through 7 are also plotted in figure 1. For some elements (for example, boron and silver), yields could not be calculated because elemental concentrations in the reference sediment were not reported. In these cases, the digestate concentrations can be used to compare different digest procedures.

Linear regression analysis and statistical tests were used to establish the bias and variability of the HNO_3 in-bottle procedure. All the mean percentage yields listed in tables 5 through 7, regardless of the element or method of analysis, were treated as a single data set for a given synthetic whole-water sample. Statistical results are listed in table 8 and the regression lines are shown in figures 2 through 4.

Because the yield data range over a wide percentage, the authors used linear regression analysis to calculate the slope, *y*-intercept, and coefficient of determination (R^2) for the equation describing the relation between percentage yield from the HNO_3 in-bottle digestion to the HCl in-bottle digestion. A slope coefficient of one and a *y*-intercept of zero indicate exact correlation. The corresponding p-values indicate the degree of confidence in each coefficient. For additional confirmation, the One-Sample Sign Test or the Student *t*-Test, depending on whether the data set was normally distributed with equal variance, was used to test the null hypothesis. The null hypothesis tested whether the percentage yields for the HNO_3 in-bottle digestion are significantly different than the percentage yields for the HCl in-bottle digestion. The p-values were calculated for each synthetic whole-water sample to provide a level of confidence in accepting the null hypothesis. The larger the p-value the greater the confidence in accepting the null hypothesis. When the p-value exceeds 0.05, the null hypothesis is acceptable at the 95-percent confidence level.

Slope coefficients indicate that the HNO_3 in-bottle procedure provides percentage yields that are 5 to 20 percent lower than the HCl in-bottle procedure, depending on the type of synthetic whole-water sample (see table 8). For every synthetic whole-water sample tested, most elemental results are highly correlated and within the 95-percent confidence limit (see figs. 2–4). The One-Sample Sign Test or the Student *t*-Test results shown in table 8 indicate that there is a statistically significant difference (p-value less than 0.05) between percentage yields, depending on the acid used for the in-bottle digestion.

Percentage yields for the Buffalo River Sediment synthetic whole-water sample indicated that the difference between the HCl and HNO_3 in-bottle procedures is less than 10 percent for all the elements except for selenium (fig. 1). All elemental percentage yields for the Estuarine Sediment synthetic whole-water samples are within 10 percent of the

Table 2. Elemental concentrations in various digestates of a synthetic whole-water sample made from National Institute of Standards and Technology Standard Reference Material 2704, Buffalo River Sediment

[Cert., certified concentration in units provided for each element. Concentrations in parentheses are uncertified; Digestate concentration is the elemental concentration recovered by the digestion relative to the weight of the sediment used to prepare the synthetic standard; HCl, hydrochloric acid (HCl) in-bottle digestion with or without the HCl removed by evaporation; HNO_3, nitric acid in-bottle digestion; USEPA, U.S. Environmental Protection Agency's digestion procedure with or without the HCl removed by evaporation; µg/g, micrograms per gram; mg/g, milligrams per gram; ±, plus or minus; the number following the ± is the standard deviation of four separate digestions; na, not available]

Element	Cert.	Digestate concentration		
		HCl	HNO_3	USEPA
Aluminum, mg/g	61.1	6.55±0.09	7.4±0.2	12.4±0.6
Antimony, µg/g	3.79	1.92±0.03	1.88±0.04	1.3±0.2
Arsenic, µg/g	23.4	14.3±0.2	13.4±0.1	18.5±0.7
Barium, µg/g	414	79±3	81±2	91.2±0.5
Beryllium, µg/g	na	0.52±0.02	0.52±0.03	0.66±0.03
Boron, µg/g	na	8.0±0.4	6.7±0.4	16±5
Cadmium, µg/g	3.45	3.20±0.03	3.11±0.01	3.44±0.02
Calcium, mg/g	26	22.6±0.6	22.0±0.1	23.1±0.1
Chromium, µg/g	135	63.8±0.7	66.0±0.6	82±2
Cobalt, µg/g	14.0	10.7±0.1	9.7±0.1	12.0±0.4
Copper, µg/g	98.6	79±2	77±1	90±5
Iron, mg/g	41.1	19.9±0.6	18.7±0.2	29.1±0.9
Lead, µg/g	161	164±1	148±6	146±8
Lithium, µg/g	(50)	15.9±0.2	16.5±0.3	25.8±0.8
Magnesium, mg/g	12.0	7.2±0.2	6.90±0.01	8.4±0.1
Manganese, µg/g	555	400±6	392±4	490±10
Molybdenum, µg/g	na	1.25±0.08	0.90±0.07	3.2±0.3
Nickel, µg/g	44.1	28.7±0.6	26.4±0.4	34±1
Potassium, mg/g	20.0	1.4±0.1	1.48±0.04	1.9±0.2
Selenium, µg/g	(1.1)	0.8±0.1	0.44±0.08	0.8±0.1
Silica, SiO_2, mg/g	622	21±2	20.7±0.5	30±1
Silver, µg/g	na	0.35±0.03	0.31±0.04	0.35±0.02
Sodium, mg/g	5.47	0.20±0.01	0.20±0.01	0.30±0.01
Strontium, µg/g	(130)	39.0±0.4	35.5±0.7	40.0±0.9
Thallium, µg/g	1.2	0.57±0.01	0.55±0.01	0.60±0.02
Uranium, µg/g	3.13	0.49±0.01	0.50±0.02	0.66±0.05
Vanadium, µg/g	95	14.7±0.1	13.8±0.4	21±1
Zinc, µg/g	438	340±10	293±4	390±20

Table 3. Elemental concentrations in various digestates of a synthetic whole-water sample made from National Institute of Standards and Technology Standard Reference Material 1645, Riverine Sediment

[Cert., certified concentration in units provided for each element. Concentrations in parentheses are uncertified; Digestate concentration is the elemental concentration recovered by the digestion relative to the weight of the sediment used to prepare the synthetic standard; HCl, hydrochloric acid (HCl) in-bottle digestion with or without the HCl removed by evaporation; HNO_3, nitric acid in-bottle digestion; USEPA, U.S. Environmental Protection Agency's digestion procedure with or without the HCl removed by evaporation; µg/g, micrograms per gram; mg/g, milligrams per gram; ±, plus or minus; the number following the ± is the standard deviation of four separate digestions; na, not available; nd, not detected]

Element	Cert.	Digestate concentration		
		HCl	HNO_3	USEPA
Aluminum, mg/g	22.6	3.37±0.01	2.77±0.01	4.0±0.3
Antimony, µg/g	(51)	19.2±0.5	13.3±0.5	17±1
Arsenic, µg/g	(66)	53±3	36.6±0.9	45±1
Barium, µg/g	na	61.5±0.1	48±1	56±2
Beryllium, µg/g	na	0.58±0.01	0.43±0.01	0.53±0.02
Boron, µg/g	na	20.5±0.4	15.0±0.2	16.3±0.9
Cadmium, µg/g	10.2	10.0±0.1	7.73±0.03	8.79±0.05
Calcium, mg/g	(29)	32.6±0.3	26.0±0.5	27.6±0.4
Chromium, mg/g	29.6	31.2±0.7	25.5±0.1	27±1
Cobalt, µg/g	10.1	6.6±0.1	4.80±0.05	5.7±0.1
Copper, µg/g	109	111±6	86.1±0.3	94±3
Iron, mg/g	113	53.1±0.8	38±9	64±4
Lead, µg/g	714	750±20	641.1±0.4	650±10
Lithium, µg/g	na	2.19±0.04	1.61±0.01	2.6±0.2
Magnesium, mg/g	7.4	7.8±0.1	6.1±0.2	6.5±0.1
Manganese, µg/g	785	580±20	420±3	540±20
Molybdenum, µg/g	na	9.9±0.2	6.6±0.1	10.4±0.8
Nickel, µg/g	45.8	35.4±0.7	26±2	30±1
Potassium, mg/g	12.6	0.42±0.03	0.34±0.01	0.58±0.05
Selenium, µg/g	(1.5)	0.87±0.08	0.37±0.03	0.46±0.04
Silica, SiO_2, mg/g	na	13.9±0.2	11.0±0.1	15.1±0.3
Silver, µg/g	na	1.8±0.2	1.4±0.3	1.41±0.09
Sodium, mg/g	5.4	1.20±0.01	1.00±0.01	1.10±0.01
Strontium, µg/g	na	900±30	727±1	710±30
Thallium, µg/g	1.44	1.55±0.01	1.18±0.03	1.13±0.01
Uranium, µg/g	1.11	0.80±0.02	0.65±0.01	0.77±0.02
Vanadium, µg/g	23.5	nd	nd	nd
Zinc, µg/g	1.72	1,640±40	1,234±6	1,530±70

Table 4. Elemental concentrations in various digestates of a synthetic whole-water sample made from National Institute of Standards and Technology Standard Reference Material 1646, Estuarine Sediment

[Cert., certified concentration in units provided for each element. Concentrations in parentheses are uncertified; Digestate concentration is the elemental concentration recovered by the digestion relative to the weight of the sediment used to prepare the synthetic standard; HCl, hydrochloric acid (HCl) in-bottle digestion with or without the HCl removed by evaporation; HNO_3, nitric acid in-bottle digestion; USEPA, U.S. Environmental Protection Agency's digestion procedure with or without the HCl removed by evaporation; µg/g, micrograms per gram; mg/g, milligrams per gram; ±, plus or minus; the number following the ± is the standard deviation of four separate digestions; na, not available]

Element	Cert.	Digestate concentration		
		HCl	HNO_3	USEPA
Aluminum, mg/g	62.5	7.2±0.1	7.2±0.1	14±1
Antimony, µg/g	(0.4)	0.06±0.01	0.07±0.01	0.03±0.01
Arsenic, µg/g	11.6	7.72±0.05	7.34±0.05	8.13±0.09
Barium, µg/g	na	29.9±0.4	30.2±0.9	40±1
Beryllium, µg/g	(1.5)	0.53±0.02	0.50±0.01	0.72±0.02
Boron, µg/g	na	25.3±0.6	25.4±0.1	29.8±0.9
Cadmium, µg/g	0.36	0.37±0.07	0.33±0.01	0.34±0.01
Calcium, mg/g	8.3	3.30±0.01	3.30±0.01	3.7±0.1
Chromium, µg/g	76	25.6±0.3	25.4±0.3	31.4±0.6
Cobalt, µg/g	10.5	6.65±0.09	6.07±0.03	6.92±0.08
Copper, µg/g	18	11.7±0.1	11.6±0.1	13.3±0.2
Iron, mg/g	33.5	18.6±0.1	18.1±0.1	22.6±0.4
Lead, µg/g	28.2	21.3±0.2	18.5±0.3	16.3±0.2
Lithium, µg/g	(49)	16.8±0.2	16.3±0.2	24.4±0.9
Magnesium, mg/g	10.9	6.00±0.02	5.90±0.01	7.1±0.1
Manganese, µg/g	375	185±3	173±2	216±2
Molybdenum, µg/g	(2.0)	1.00±0.02	0.86±0.02	1.14±0.03
Nickel, µg/g	32	15.8±0.2	14.9±0.1	18.8±0.3
Potassium, mg/g	(14)	3.13±0.04	3.1±0.1	3.9±0.1
Selenium, µg/g	(0.6)	0.67±0.03	0.69±0.05	0.60±0.03
Silica, SiO_2, mg/g	(663)	30±1	28.9±0.7	35±5
Silver, µg/g	na	0.11±0.02	0.10±0.01	0.12±0.01
Sodium, mg/g	(20)	10.1±0.1	10.0±0.1	10.6±0.1
Strontium, µg/g	na	29.3±0.2	27.8±0.2	29.5±0.6
Thallium, µg/g	(0.5)	0.15±0.01	0.13±0.01	0.13±0.01
Uranium, µg/g	na	1.10±0.01	1.02±0.01	1.09±0.02
Vanadium, µg/g	94	35.8±0.7	34.6±0.4	37.9±0.6
Zinc, µg/g	138	92.4±0.5	82.6±0.7	98±1

Table 5. Percentage yield for a synthetic whole-water sample made from National Institute of Standards and Technology Standard Reference Material 2704, Buffalo River Sediment, using various digestion procedures

[HCl, hydrochloric acid (HCl) in-bottle digestion with or without the HCl removed by evaporation; USEPA, U.S. Environmental Protection Agency's digestion procedure with or without the HCl removed by evaporation; HNO_3, nitric acid in-bottle digestion; ±, plus or minus; the number following the ± is the standard deviation of four separate digestions]

Element	Buffalo River Sediment, in percentage yield		
	HCl	HNO_3	USEPA
Aluminum	10.7±0.2	12.2±0.4	20±1
Antimony	50.7±0.8	50±1	35±4
Arsenic	61.2±0.9	57.1±0.6	79±3
Barium	19.2±0.8	19.5±0.5	22.0±0.1
Cadmium	92.7±0.9	90.3±0.1	99.7±0.5
Calcium	87±2	84.6±0.4	89±1
Chromium	47.3±0.5	48.9±0.5	61±1
Cobalt	76.5±0.8	69.2±0.9	86±3
Copper	80±2	78±1	92±5
Iron	48±1	45.6±0.5	71±2
Lead	102.2±0.9	92±4	91±5
Lithium	31.9±0.4	33.0±0.6	52±2
Magnesium	60±2	57.1±0.2	69.9±0.9
Manganese	72±1	70.5±0.6	88±2
Nickel	65±1	59.9±0.9	78±3
Potassium	6.8±0.7	7.4±0.2	9.7±0.8
Selenium	80±10	40±7	70±10
Silica, SiO_2	3.4±0.3	3.3±0.1	4.8±0.2
Sodium	4.1±0.4	3.7±0.2	6.1±0.2
Strontium	30.0±0.3	27.3±0.5	30.8±0.7
Thallium	47.2±0.4	46±1	50±2
Uranium	15.8±0.2	16.1±0.5	21±2
Vanadium	15.5±0.1	14.5±0.4	22±1
Zinc	76±2	66.9±0.9	89±4

HCl in-bottle yields. In contrast, the HNO_3 in-bottle yields for the Riverine Sediment synthetic whole-water samples are 11 to 30 percent lower than for the HCl in-bottle results for 16 of the 26 elements determined. Such differences underscore the dependence of percentage yield on sediment composition.

For most elements, the USEPA digestion procedure provided higher percentage yields than both in-bottle procedures. The USEPA percentage yields, however, are also dependent on the composition of the whole-water matrix. The higher yields primarily are related to differences in the digestion procedure. Samples are heated at 85°C until the solution is reduced by 80 percent. The remaining solution is covered and refluxed at the same temperature for 30 minutes, diluted to volume, and analyzed. The increases in acid concentration and temperature during the reflux step enhance dissolution of refractory elements compared to the in-bottle digestion procedures.

The variability in both in-bottle digestion procedures was similar. Variability for the HNO_3 in-bottle procedure ranged from 0.1 to 8

Table 6. Percentage yield for a synthetic whole-water sample made from National Institute of Standards and Technology Standard Reference Material 1645, Riverine Sediment, using various digestion procedures

[HCl, hydrochloric acid (HCl) in-bottle digestion with or without the HCl removed by evaporation; USEPA, U.S. Environmental Protection Agency's digestion procedure with or without the HCl removed by evaporation; HNO_3, nitric acid in-bottle digestion; ±, plus or minus; nd, not detected, less than the method detection limit; the number following the ± is the standard deviation of four separate digestions]

Element	Riverine Sediment, in percentage yield		
	HCl	HNO_3	USEPA
Aluminum	15.0±0.1	12.6±0.3	18±1
Antimony	38±1	26.7±0.8	34±2
Arsenic	81±2	56±1	68±2
Cadmium	99±1	75.8±0.3	86±2
Calcium	112±1	90±2	95.1±0.6
Chromium	103±3	85±2	91±3
Cobalt	65±1	47.4±0.3	56±1
Copper	101±4	77±2	86±3
Iron	47.0±0.7	33.2±0.8	58±2
Lead	104±2	88±2	91±2
Magnesium	106±1	83±2	87.8±0.9
Manganese	73±2	52±1	68±2
Nickel	75±3	58±3	65±3
Potassium	3.4±0.2	2.7±0.1	4.7±0.4
Selenium	54±6	24±3	31±2
Sodium	23.0±0.2	18.2±0.1	20.5±0.1
Thallium	108.2±0.7	82±1	78.4±0.2
Uranium	72±1	58.7±0.6	70±2
Vanadium	nd	nd	nd
Zinc	95±2	71±1	89±4

percent for four replicate digestions of all three synthetic whole-water samples. By comparison, the variability in results with similar percentage yield is greater for selected elements when using the USEPA procedure. This increase in variability is caused by the difficulty in controlling digestate volumes and heating conditions during the refluxing step.

Elements that are most likely to be adsorbed to the particulate coatings, for example, cadmium, cobalt, copper, lead, manganese, and nickel, give higher percentage yields. Elements that predominately compose the sediment's mineral substrate, such as aluminum, iron, potassium, silica, and sodium, give much lower percentage yields.

An anomaly was also identified when comparing whole-water recoverable arsenic results from HG–AAS to those from ICP–MS. Arsenic results from HG–AAS were 20 to 50 percent lower for all synthetic whole-water digestates reported here. In addition, arsenic results for USGS Standard Reference Water Sample WW-1, a synthetic whole-water standard, averaged 5±1 µg/L for four determinations as compared to the published most probable value of 20 µg/L (the ICP–MS yielded 18.13±0.09 µg/L). The HG–AAS concentrations are most likely lower because particulate material might settle out in the sample tube before sample introduction. This

Table 7. Percentage yield for a synthetic whole-water sample made from National Institute of Standards and Technology Standard Reference Material 1646, Estuarine Sediment, using various digestion procedures

[HCl, hydrochloric acid (HCl) in-bottle digestion with or without the HCl removed by evaporation; USEPA, U.S. Environmental Protection Agency's digestion procedure with or without the HCl removed by evaporation; HNO_3, nitric acid in-bottle digestion; ±, plus or minus; the number following the ± is the standard deviation of four separate digestions]

Element	Estuarine Sediment, in percentage yield		
	HCl	HNO_3	USEPA
Aluminum	11.5±0.2	11.6±0.2	23±2
Antimony	15.8±0.7	16.9±0.7	8±1
Arsenic	66.6±0.5	63.3±0.4	70.0±0.8
Beryllium	35±2	33.6±0.6	48±2
Cadmium	100±20	92±3	96±2
Calcium	39.8±0.1	39.4±0.3	100±20
Chromium	33.7±0.4	33.5±0.4	41.3±0.8
Cobalt	63.3±0.8	57.8±0.3	65.9±0.7
Copper	64.9±0.4	64.5±0.7	74±1
Iron	55.7±0.2	54.1±0.4	32±5
Lead	75.5±0.6	66±1	57.9±0.9
Lithium	34.3±0.4	33.4±0.5	50±2
Magnesium	55.0±0.2	53.7±0.4	28±5
Manganese	49.3±0.8	46.1±0.5	57.6±0.5
Molybdenum	49.9±0.9	43±1	57±2
Nickel	49.5±0.5	46.7±0.2	58.9±0.9
Potassium	22.3±0.3	22.3±0.4	28.0±0.7
Selenium	112±5	114±8	100±5
Silica, SiO_2	4.6±0.2	4.4±0.1	1.6±0.3
Sodium	50.5±0.2	50.2±0.3	53.2±0.6
Thallium	29.4±0.4	26.1±0.3	25.8±0.4
Vanadium	38.1±0.7	36.8±0.5	40.3±0.7
Zinc	66.9±0.4	59.8±0.5	71.2±0.9

settling effect is worsened for the synthetic whole-water samples because they have sediment concentrations that are greater than those normally present in natural-water samples submitted to NWQL.

CONCLUSIONS

The advantages and disadvantage of using HNO_3 instead of HCl for the in-bottle digestion are summarized below.

Advantages of using the HNO_3 in-bottle digestion procedure:

- The digestate is compatible with all current (1999) USGS analytical methods used to determine aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, calcium, chromium, cobalt, copper, iron, lead, lithium, magnesium, manganese, molybdenum, nickel, potassium, selenium, silica, silver, sodium, strontium, thallium, uranium, vanadium, and zinc.
- The variability of 0.1 to 8 percent is comparable to the HCl in-bottle digestion procedure.

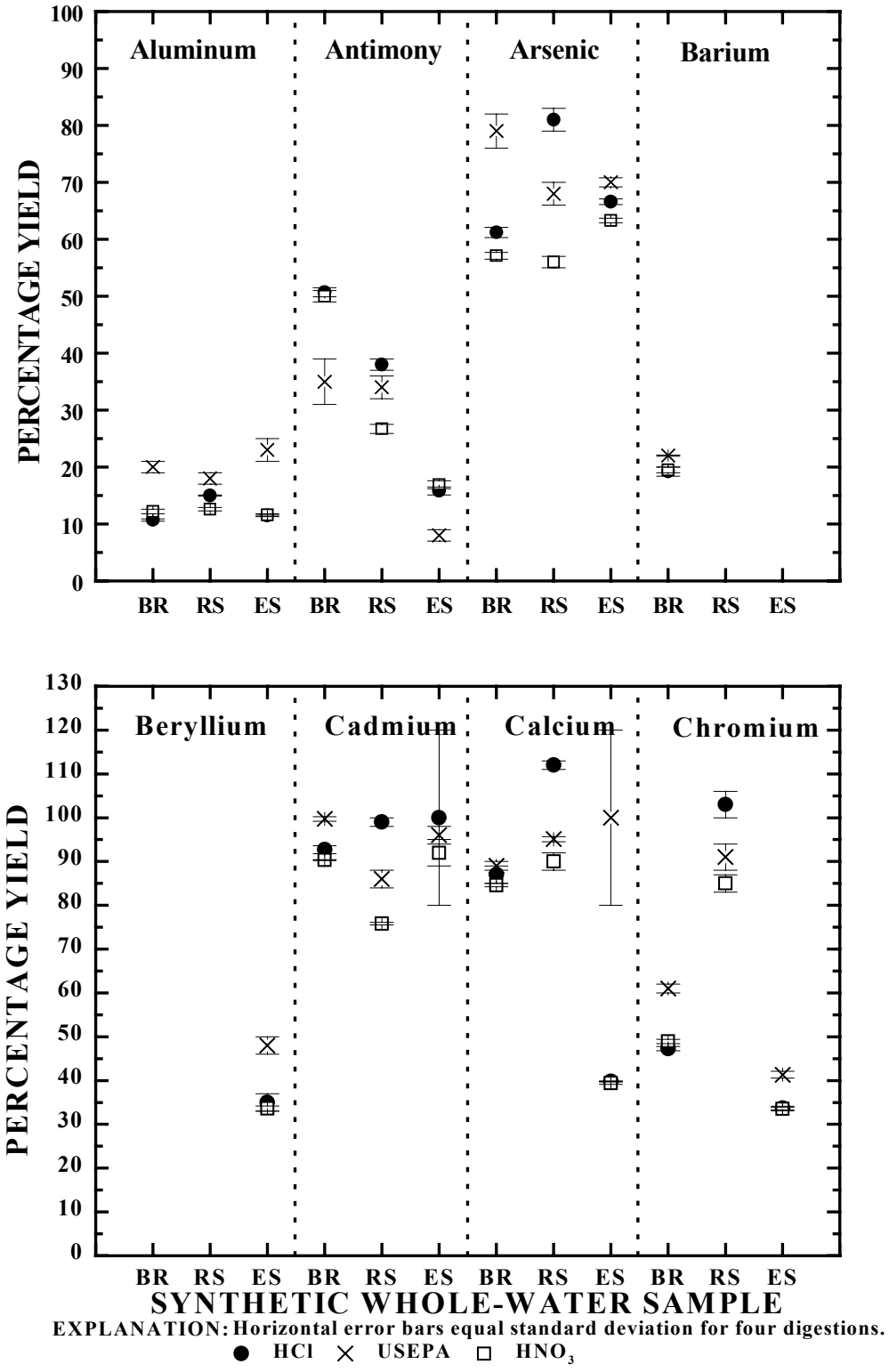
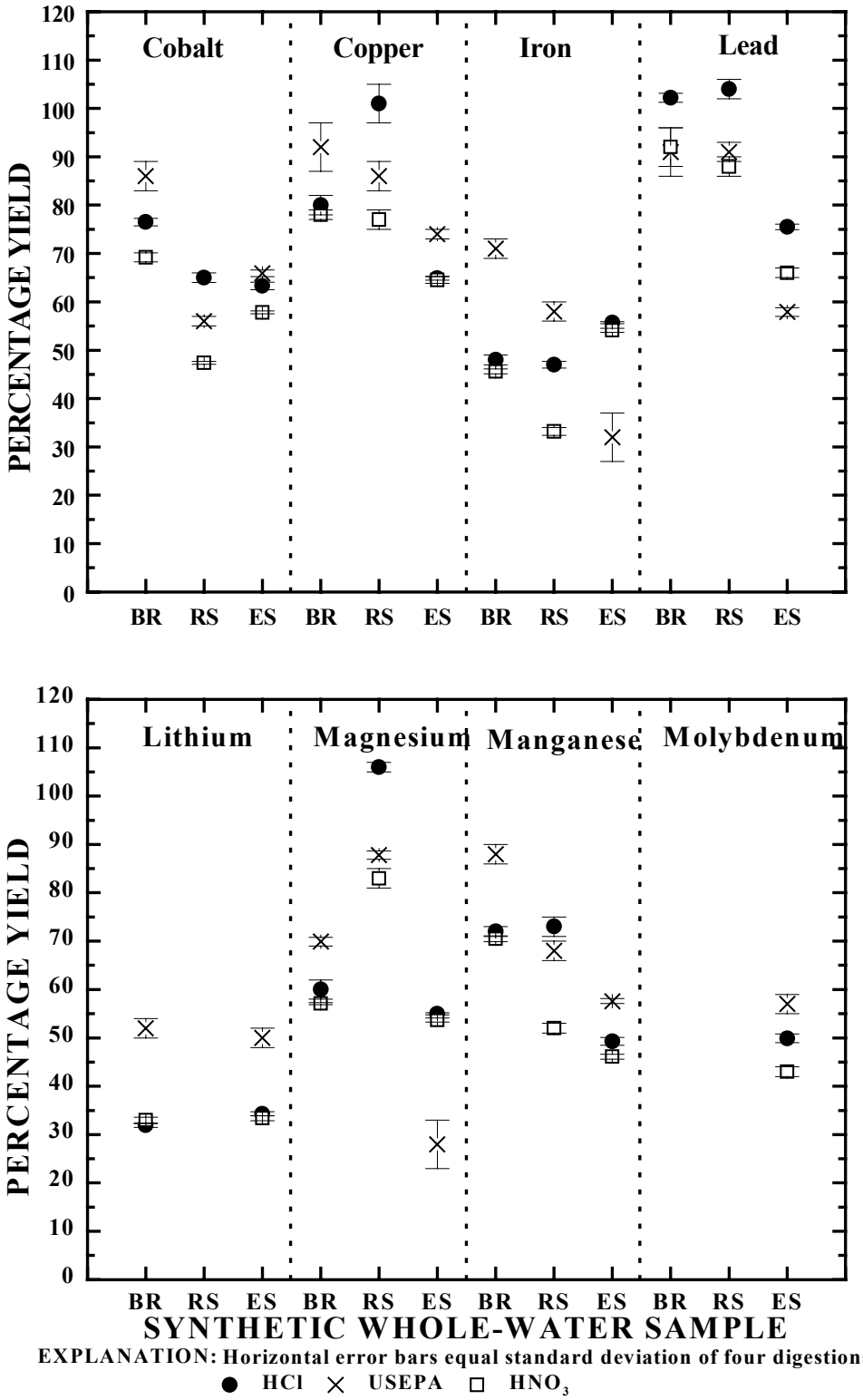


Figure 1. Percentage yield as a function of hydrochloric acid in-bottle digestion (HCl), U.S. Environmental Protection Agency digestion (USEPA), and nitric acid in-bottle digestion (HNO_3) procedures for synthetic whole-water samples prepared using Buffalo River (BR), Riverine (RS), and Estuarine (ES) Sediments.



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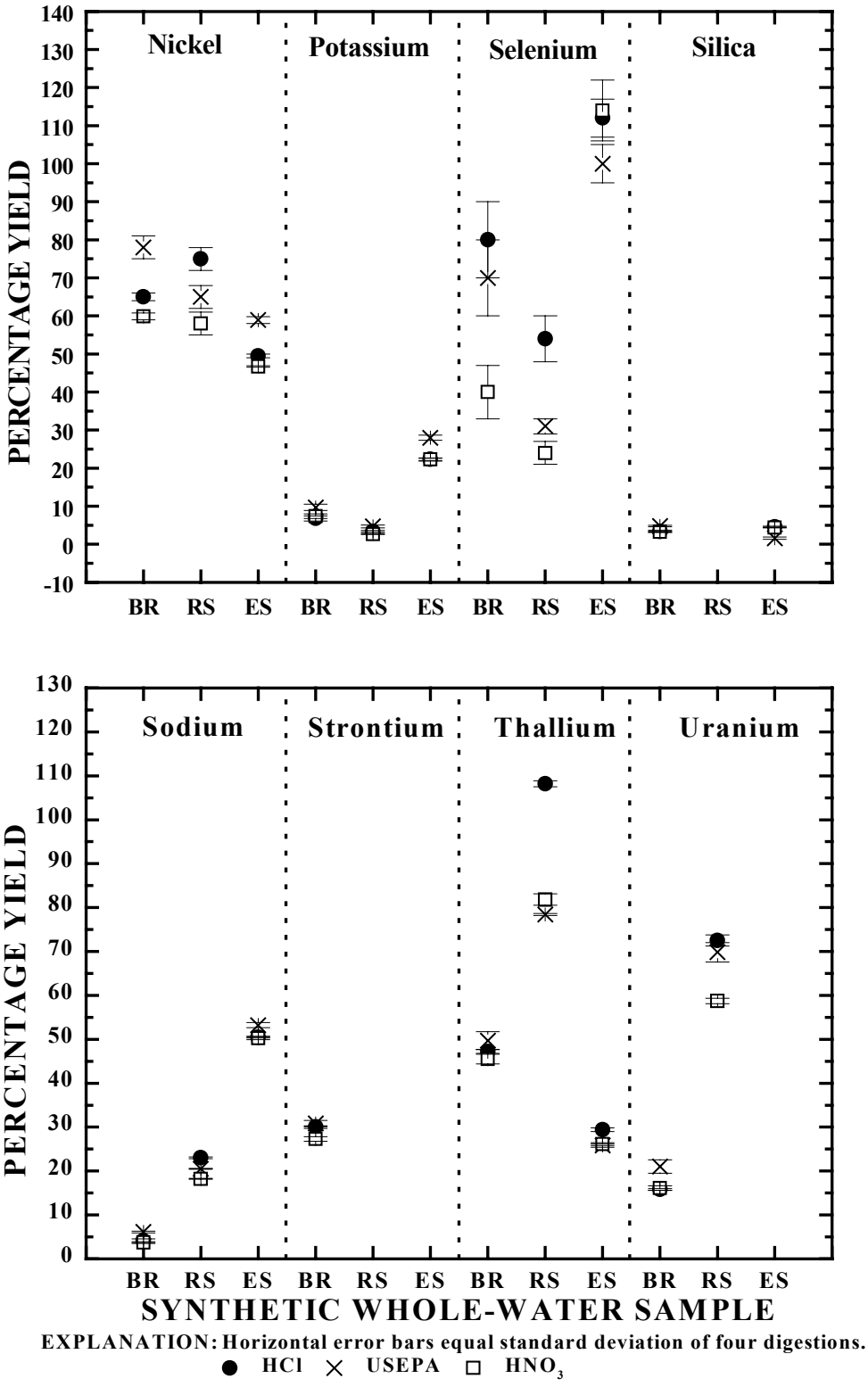

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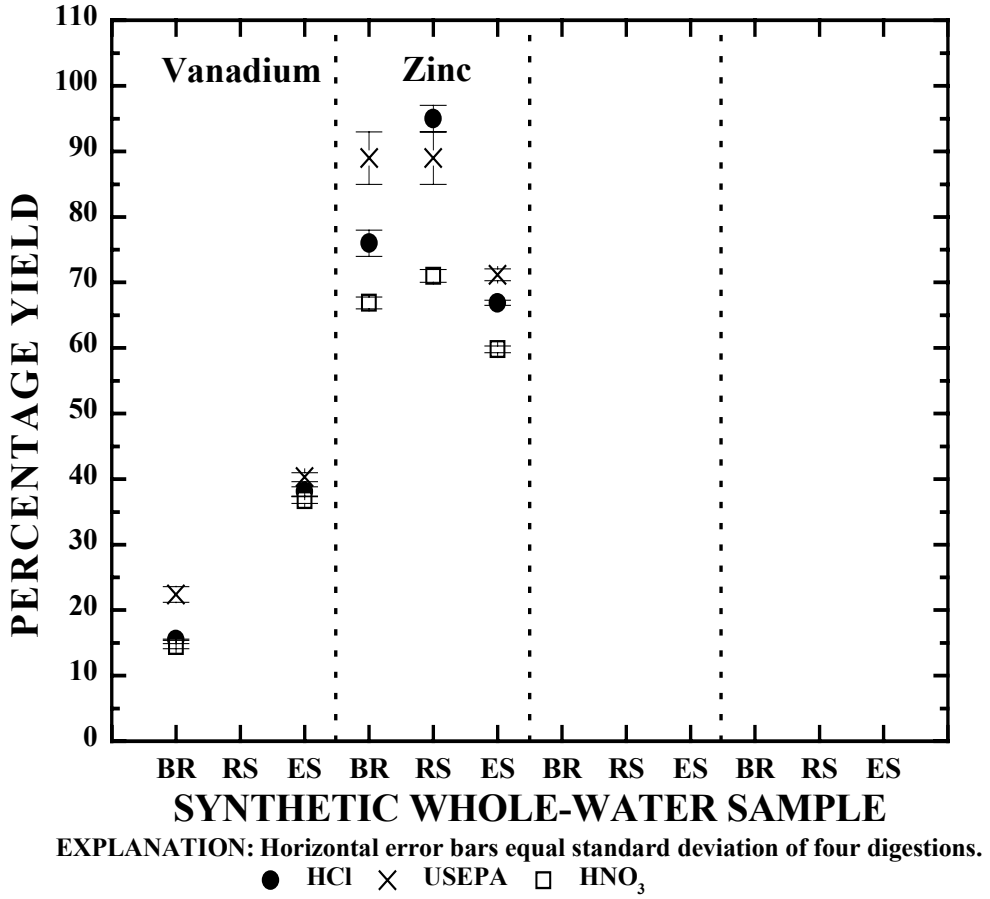

Figure 1. Percentage yield as a function of hydrochloric acid in-bottle digestion (HCl), U.S. Environmental Protection Agency digestion (USEPA), and nitric acid in-bottle digestion (HNO_3) procedures for synthetic whole-water samples prepared using Buffalo River (BR), Riverine (RS), and Estuarine (ES) Sediments—Continued.

- The procedure uses less chemical reagents and, therefore, produces less chemical waste for some analytical methods.

- Interferences from chloride are reduced.

Disadvantage of using the HNO_3 in-bottle digestion procedure:

- Results from the synthetic whole-water samples indicate that the HNO_3 in-bottle procedure might give negatively biased recoverable concentrations relative to the HCl in-bottle procedure. Recoverable concentrations are dependent on the composition of the particulate matter in the whole-water sample regardless of the digestion procedure used.

The three acid-digestion procedures tested do not completely solubilize all elements that were determined. If a total (100 percent) digestion is required for any element in a whole-water sample, then it can be argued that none of these methods will be satisfactory. However, if a recoverable elemental concentration (less than 100 percent) is

Table 8. Statistical analysis summary of elemental percentage yield for the nitric acid in-bottle digestion in relation to the hydrochloric acid in-bottle digestion

[BR, National Institute of Standards and Technology Standard Reference Material 2704, Buffalo River Sediment; RS, National Institute of Standards and Technology Standard Reference Material 1645, Riverine Sediment; ES, National Institute of Standards and Technology Standard Reference Material 1646, Estuarine Sediment; p-value, level of significance; R^2, coefficient of determination; n, number of data points; <, less than]

Regression analysis

	Slope		*y*-intercept			
	Coefficient	p-value [a]	Coefficient	p-value [b]	R^2	n
BR	0.88	<0.0001	2.4	0.4372	0.9296	24
RS	0.81	<0.0001	-3.9	0.2011	0.9667	19
ES	0.95	<0.0001	0.1	0.9345	0.9875	23

Statistical tests

	Test	Statistic	p-value [c]	n
BR	One-Sample Sign Test	1.75	0.0227	24
RS	Student *t*-Test	9.32	<0.0001	19
ES	One-Sample Sign Test	1.30	0.0009	23

[a] The null hypothesis tested: slope is not equal to one.

[b] The null hypothesis tested: *y*-intercept is equal to zero.

[c] The null hypothesis tested: the medians (or means for the Student *t*-Test) of the percentage yields for the nitric acid in-bottle digestion are not significantly different from the percentage yields for the hydrochloric acid in-bottle digestion.

acceptable for a whole-water sample, then the reproducibility of the digestion procedure should be the primary concern. Both the HCl and HNO_3 in-bottle digestion procedures give excellent reproducibility for all elements determined. Therefore, the simplicity of the digestion procedure should be the primary reason for the method selected. Newer methods that analyze the digestate from the HCl in-bottle digestion procedure may require additional steps (for example, removal of HCl and the reconstitution of the residue) to eliminate interferences. Such steps increase the analysis time and chances for contamination. The HNO_3 in-bottle digestion is the preferred method for routine use at the NWQL. Nevertheless, the original HCl in-bottle digestion procedure can be used if customers require this acid-digestion procedure.

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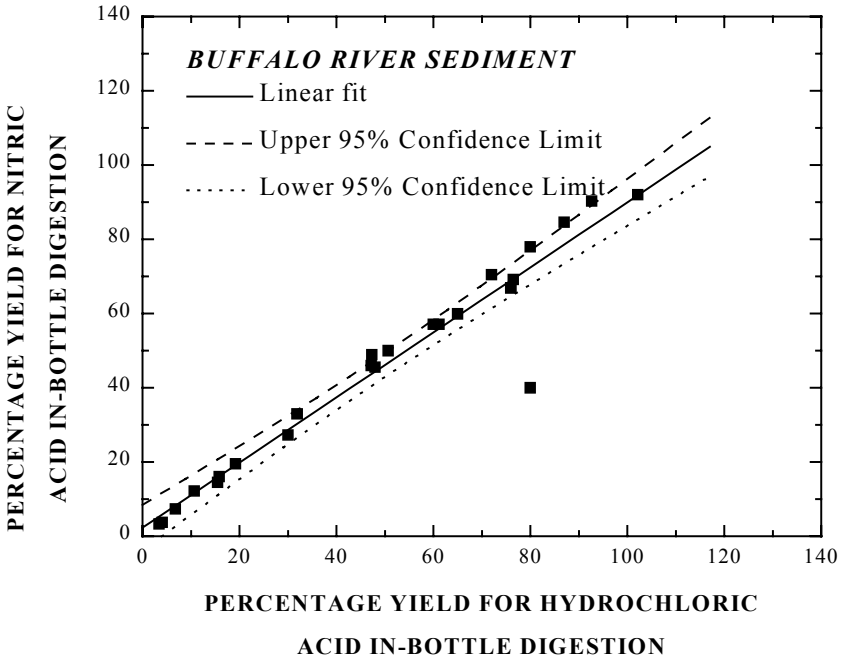

Figure 2. —Linear regression analysis of elemental percentage yield for the nitric acid in-bottle digestion in relation to the hydrochloric acid in-bottle digestion for a synthetic whole-water sample made from Buffalo River Sediment.

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APPENDIX

The presence of chloride in the HCl in-bottle and the USEPA digestates interferes with the determination of ambient concentrations of arsenic and vanadium by ICP–MS and selenium by GF–AAS. Therefore, prior to comparing the results of the HCl and HNO_3 in-bottle digestion

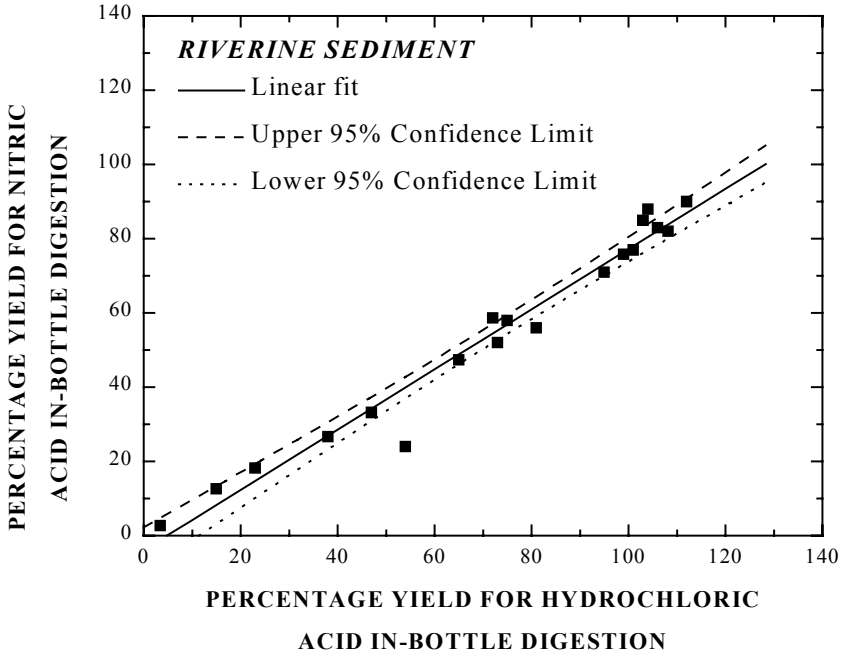

Figure 3. —Linear regression analysis of elemental percentage yield for the nitric acid in-bottle digestion in relation to the hydrochloric acid in-bottle digestion for a synthetic whole-water sample made from Riverine Sediment.

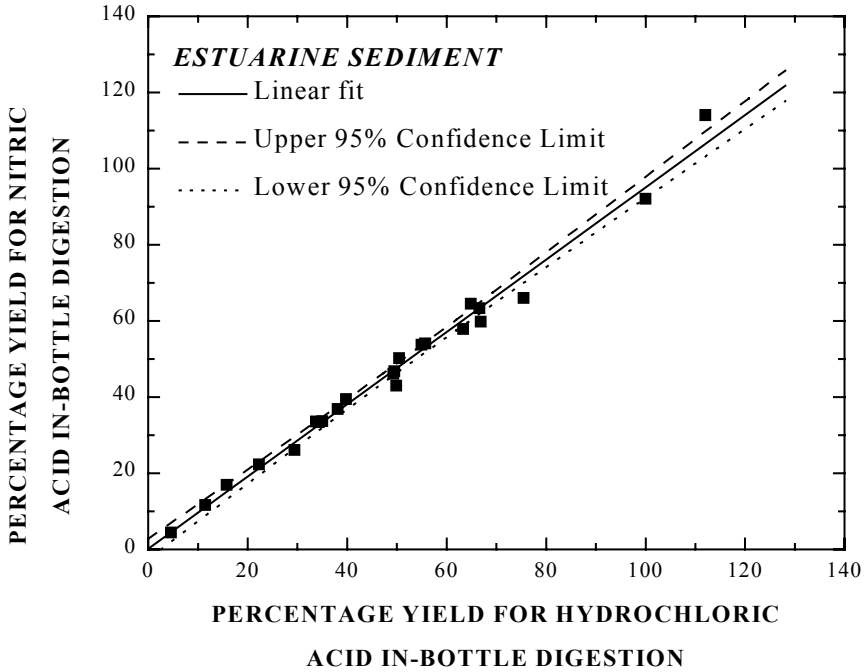

Figure 4. Linear regression analysis of elemental percentage yield for the nitric acid in-bottle digestion in relation to the hydrochloric acid in-bottle digestion for a synthetic whole-water sample made from Estuarine Sediment.

procedures, it was necessary to remove chloride from the HCl in-bottle digestates. The method used is outlined here.

Subboiling Evaporation Procedure

The high concentration of HCl in the HCl in-bottle digestates is removed through volatilization by using subboiling evaporation at 85°C. At this temperature, the risk of losing temperature-sensitive elements is minimized. The bias and variability of subboiling evaporation was determined by using results from U.S. Geological Survey Standard Reference Water Sample T123, a multielement standard (see table 9), and a synthetic whole-water sample (see table 10). Four aliquots of each digestate were evaporated on different days. Residues from the evaporation were dissolved in a calibration-blank solution before analysis by ICP–MS or ICP–AES. Results for T123 and the multielement standard show that every element is within one standard deviation of the most probable value, indicating there are no losses during the evaporation. Results for the multielement standard show that the variability of the evaporative procedure is no greater than 15 percent at about 5 μg/L. In general, data in table 10 show that the elemental concentrations determined in the synthetic whole-water HCl in-bottle digestate of the Estuarine Sediment were within the experimental error of corresponding results from the evaporated solutions.

Table 9. Bias and variability for the subboiling evaporation technique

[SRWS T123, U.S. Geological Survey Standard Reference Water Sample T123; MPV, most probable value from round-robin results using multiple analytical methods; THEO, theoretical mean and standard deviation of a multielement standard from four determinations on different days; EXP, experimental means after subboiling evaporation; na, not available; ±, plus or minus; the number following the ± in the EXP columns is the standard deviation of four aliquots evaporated and analyzed on different days]

Element	SRWS T123		Multielement standard	
	MPV	EXP	THEO	EXP
Aluminum	10±10	8.0±0.4	5.5±0.1	6±1
Antimony	7±2	6.3±0.9	6.17±0.02	5.9±0.4
Arsenic	20±2	19±2	4.93±0.08	4.5±0.4
Barium	7.6±0.9	7.1±0.5	5.0±0.1	4.8±0.3
Beryllium	8.1±0.8	7.5±0.6	4.72±0.07	4.7±0.2
Cadmium	5.9±0.9	5.3±0.4	4.9±0.5	4.9±0.5
Chromium	11±1	9.3±0.7	4.94±0.02	4.8±0.4
Cobalt	5.3±0.8	5.7±0.6	5.23±0.07	5.5±0.7
Copper	10±1	9.6±0.3	4.8±0.2	4.7±0.5
Lead	10±2	9.7±0.7	5.09±0.06	4.8±0.4
Manganese	14±1	12.7±0.9	4.9±0.2	5.0±0.4
Molybdenum	9±1	9±1	5.53±0.09	5.0±0.5
Nickel	4±1	4.2±0.4	4.7±0.3	4.5±0.5
Silver	1.4±0.6	1.4±0.2	na	na
Strontium	49±3	46±3	na	na
Thallium	na	na	5.4±0.4	4.9±0.4
Uranium	na	na	5.16±0.07	5.0±0.4
Vanadium	4±1	4.0±0.7	5.5±0.4	4.8±0.4
Zinc	6±4	6.7±0.7	5.1±0.3	6.1±0.4

Table 10. Bias and variability of subboiling evaporation of digestate from a synthetic whole-water sample made from National Institute of Standards and Technology Standard Reference Material 1646, Estuarine Sediment

[µg/g, micrograms per gram; mg/g, milligrams per gram; HCl, hydrochloric acid (HCl) in-bottle digestate; -HCl, subboiling evaporation of HCl in-bottle digestate; nd, not detected; ±, plus or minus; the number following the ± is the standard deviation of four aliquots evaporated and analyzed by inductively coupled plasma–atomic emission spectrometry on different days]

Element	Estuarine sediment	
	HCl	-HCl
Aluminum, mg/g	8.4±0.1	8.18±0.07
Barium, µg/g	29.5±0.5	28.0±0.3
Beryllium, µg/g	0.5±0.2	0.2±0.2
Boron, µg/g	26±3	27±3
Cadmium, µg/g	nd	nd
Calcium, mg/g	3.30±0.01	3.30±0.01
Chromium, µg/g	26.1±0.5	26±2
Cobalt, µg/g	84±4	87±7
Copper, µg/g	12±1	10.5±0.5
Iron, mg/g	18.7±0.1	18.6±0.1
Lead, µg/g	nd	nd
Lithium, µg/g	16±1	16.4±0.4
Magnesium, mg/g	6.00±0.02	6.00±0.03
Manganese, µg/g	177.6±0.6	178±1
Molybdenum, µg/g	9±2	11±7
Nickel, µg/g	16±5	20±10
Silica, SiO_2, mg/g	30±1	23.1±0.8
Silver, µg/g	nd	nd
Sodium, mg/g	10.10±0.05	9.99±0.03
Strontium, µg/g	26.8±0.1	26.3±0.2
Vanadium, µg/g	28.2±0.6	28.6±0.7
Zinc, µg/g	92±6	93±6

The entire evaporative procedure is conducted inside a laminar-flow clean bench. Details of the evaporative procedure are outlined as follows:

- Weigh a 25- to 50-g aliquot of in-bottle digestate (Hoffman and others, 1996) into a 50-mL Teflon centrifuge tube.

NOTE 4: Prepare a reagent blank and a standard reference material with each set of samples evaporated.

- Place the centrifuge tube in a graphite-block heater that is thermostatically heated to 85°C [see Hoffman and others (1996) for a description of the graphite-block heater]. Heat to dryness (takes less than 8 hours for a set of 12 samples); cool.

- Reconstitute the sample residue to its original weight with the calibration blank solution specified in the analytical method being used for quantitation.